Comment on "Quality Assessment Algorithm for Vapor−Liquid Equilibrium Data" (Kang, J. W.; Diky, V.; Chirico, R. D.; Magee, J. W.; Muzny, C. D.; Abdulagatov, I.; Kazakov, A.F.; Frenkel, M. *J. Chem. Eng. Data* 2010, *55*, 3631−3640)

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Jeong Won Kang et al. have recently published an additional procedure for testing the thermodynamic consistency of vapor−liquid equilibria (VLE) data.[1] It is the purpose of this communication to correct certain statements it contains regarding our results and add some additional information.

(1) In the section about the Herington test, it is stated that "Wisniak slightly modified the criteria provided by Herington... The test criteria are met for isothermal data sets with $D < 5$, while for isobaric data sets, the condition for passing is $|D - J| < 5$". The paper by Kang et al. indicates that this information comes from reference 11 (reference 2 given below). These statements are totally incorrect; they do not appear in the reference quoted. Reference 11 is a new test ($L-W$ test) for thermodynamic consistency that has no relation to the Herington test and does not require the values of areas in the Redlich−Kister graph to be carried out. The test is developed from the fundamental equation $\Delta G^{E}/RT = \sum x_i \ln \gamma_i$ and leads to a relation that can be used as *both* a point-to-point test and a global test. In this test, parameter D represents $D = 100(|L - W|)/(|L + W|)$ and is totally different from the one used in the Herington (and other) tests. The only thermal information it requires is *heats of vaporization and not heats of mixing*. Reference 11 (2 below) indicates that the limit for the deviation D is "arbitrary and will depend on the needs for which the data are required. The errors involved in the experimental data required to evaluate L and W are similar to those present in the area and Herington tests for consistency; and hence it is estimated that values of D less than 3−5 will indicate thermodynamic consistency. The higher limit is proposed for the case where the heats of vaporization are not available and must be estimated".

(2) The Herington test of consistency was widely used in the past because of its easy application and because it would declare as consistent may sets of data that were not. The derivation of the test was examined by Wisniak[3] and shown to contain a series of errors, which made its use *inappropriate* for testing VLE data (this reference does not appear in the paper by Kang et al.). These errors arose from the very limited experimental information that was available to Herington at his time. The most fundamental one was to assume that the ratio $\Delta H_M/\Delta G_M^E$ would rarely exceed the value 3.0 (where ΔH_M and ΔG_M^E are the maximum/minimum values of the heat of mixing and the excess Gibbs energy). The extensive database used by Wisniak showed that the ratio $\Delta H_M/\Delta G_M^E$ could actually reach values up to 28.6, and the value 3.0 was exceeded in more than 20 % of the cases examined.

The paper by Kang et al. proposes a quality factor for the Herington test (eqs 10 and 11 in the paper), which is based on a J factor that has no connection to experimental evidence, and hence, its use can hardly be recommended.

An in-depth analysis of the available tests for thermodynamic consistency has been published by Wisniak, Apelblat, and Segura.[4]

Literature Cited

(1) Kang, J. W.; Diky, V.; Chirico, R. D.; Magee, J. W.; Muzny, C. D.; Abdulagatov, I.; Kazakov, A. F.; Frenkel, M. Quality Assessment Algorithm for Vapor-Liquid Equilibrium Data. *J. Chem. Eng. Data* **2010**, *55*, 3631–3640.

(2) Wisniak, J. A New Test for the Thermodynamic Consistency of Vapor-Liquid Equilibrium. *Ind. Eng. Chem. Res.* **1993**, *32*, 1531–1533.

(3) Wisniak, J. The Herington Test for Thermodynamic Consistency. *Ind. Eng. Chem. Res.* **1994**, *33*, 177–180.

(4) Wisniak, J.; Apelblat, A.; Segura, H. An Assessment of Thermodynamic Consistency Tests for Vapor-Liquid Equilibria. *Phys. Chem. Liq.* **1997**, *35*, 1–58.

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